



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :

C01B 7/04, 7/07

A1

(11) International Publication Number:

WO 96/15066

(43) International Publication Date:

23 May 1996 (23.05.96)

(21) International Application Number: PCT/US95/14736

(22) International Filing Date: 14 November 1995 (14.11.95)

(30) Priority Data:

08/338,858

14 November 1994 (14.11.94) US

(71) Applicant: UNIVERSITY OF SOUTHERN CALIFORNIA
[US/US]; 3716 So. Hope Street, Los Angeles, CA 90007-4344 (US).

(72) Inventors: MINET, Ronald, G.; 33 Fontaire, Coto de Caza, CA 92679 (US). TSOTSIS, Theodore, T.; 16781 Phelps Lane, Huntington Beach, CA 92649 (US). BENSON, Sidney, M.; 110 North Bundy Drive, Brentwood, CA 90049 (US). MORTENSEN, Max, K.; 1056 Capen Avenue, Walnut, CA 91789 (US).

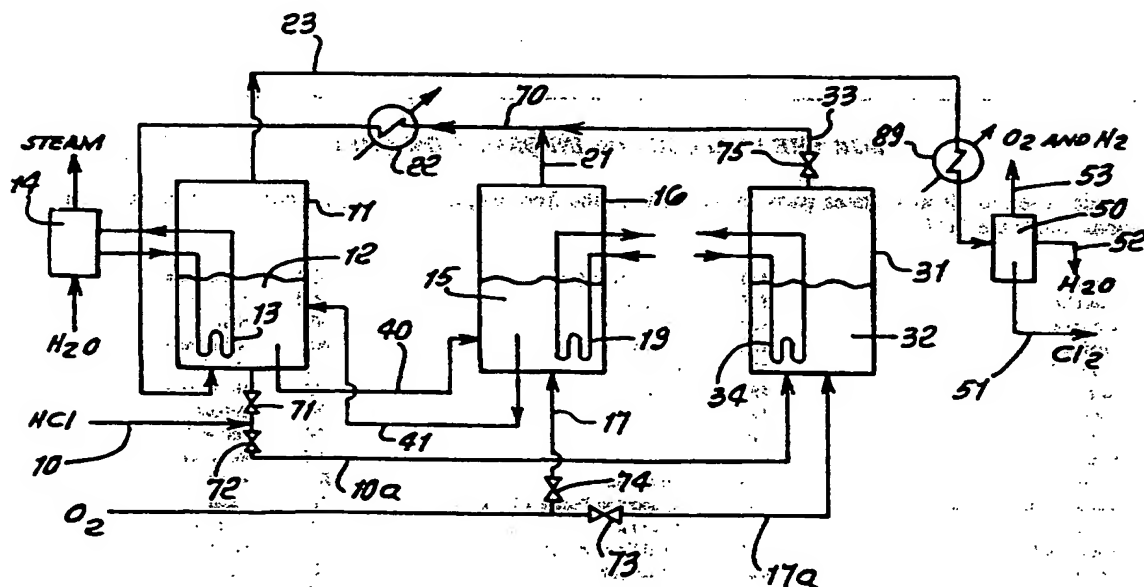
(74) Agent: ROTH, W., Norman; Roth & Goldman, Suite 707, 523 W. 6th Street, Los Angeles, CA 90014 (US).

(81) Designated States: CA, JP, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

(54) Title: RECOVERY OF CHLORINE FROM HYDROGEN CHLORIDE, WITH INTERNAL RECYCLE OF HYDROGEN CHLORIDE



(57) Abstract

A process of recovering Cl_2 from a stream of HCl (10) which comprises the steps of supplying an HCl stream (10) to a first fluidized bed of a carrier catalyst CuO (12) in a first reaction zone (11) to produce CuCl_2 , H_2O , and heat; feeding the CuCl_2 from the first zone (11) to a second reaction zone (16) via line (40); supplying O_2 (17) to the second reaction zone (16) to react with CuCl_2 in a second bed (15) at elevated temperature to produce CuO and Cl_2 ; feeding the CuO from the second bed (15) to the first bed (12) via line (41); removing Cl_2 from the second zone (16) via line (21) and recycling it via line (70) to the first reaction zone (11) for reaction with CuO at lower temperature to remove recycled HCl from the Cl_2 ; recovering the Cl_2 via line (23). A third fluidized bed is also disclosed.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

RECOVERY OF CHLORINE FROM HYDROGEN CHLORIDE, WITH INTERNAL RECYCLE OF HYDROGEN CHLORIDE

BACKGROUND OF THE INVENTION

This invention is useful in apparatus and process for the recovery of chlorine from waste or byproduct hydrogen chloride, by means of a multistage, continuous reaction process employing a combined catalytic carrier system. Hydrogen chloride is produced as a byproduct from many chemical processes, including production of titanium dioxide pigment, polyurethanes, vinyl chloride, organic chlorides, and many other useful and economically important substances. Typically, the chlorine used in the process is supplied from large-scale electrochemical plants by shipment via rail, truck or barge. The byproduct hydrogen chloride is collected and disposed of by sale at reduced price or by neutralization from some form of lime or caustic.

The described invention makes it possible to recycle the hydrogen chloride in an economical and environmentally sound manner to recover the chlorine for use in the primary process, thus materially reducing the quantity which must be shipped from outside, and at a cost which is significantly below the cost of fresh chlorine.

SUMMARY OF THE INVENTION

Basically, the process of continuously recovering chlorine from a stream of hydrogen chloride includes the steps:

a) providing a first fluidized bed of carrier catalyst, cupric oxide in a first reaction zone,

b) supplying hydrogen chloride in a first stream to the zone for reaction with cupric oxide to produce cupric chloride, water and heat, removing heat from the zone to maintain the required temperature, removing water from the zone, and removing cupric chloride from the zone,

c) feeding the cupric chloride stream to a second reaction zone, providing a second fluidized bed of cupric chloride in the second reaction zone, and

d) supplying oxygen in a third stream to the second zone for reaction with cupric chloride in the second bed at elevated temperatures to produce cupric oxide and chlorine, removing cupric oxide from the second bed for reuse as a catalyst to produce cupric chloride, and

e) removing as a fourth stream the chlorine, which contains some hydrogen chloride, from the second bed and supplying said stream to the first fluidized bed in the first reaction zone to cause the recycled hydrogen chloride to react with the cupric oxide, and thus allow the chlorine product to leave the first reaction zone substantially free from hydrogen chloride.

f) in an additional step a third reaction zone containing a third fluidized bed of cupric chloride can be provided which can be supplied with a fifth stream of oxygen and hydrogen chloride which will react to chemical equilibrium at elevated temperatures to produce chlorine, water and heat, and unconverted hydrogen chloride and oxygen, which will be removed as a sixth stream, to be supplied along the first stream of hydrogen chloride, and the fifth stream of chlorine to the first reaction zone fluidized bed, to react with cupric oxide resulting in additional production of chlorine product substantially free from hydrogen chloride.

This invention improves upon the disclosure of U.S. Patent 4,959,202, that disclosure incorporated herein by reference as background.

These and other objects and advantages of the invention, as well as the details of an illustrative embodiment, will be more fully understood from the following specification and drawings, in which:

DRAWING DESCRIPTION

- Fig. 1 is a block flow diagram;
- Fig. 2 is a material balance listing;
- Fig. 3 is a tabulation of experimental results;
- Fig. 4 is a tabulation of process economic factors;
- Fig. 5 is a tabulation of process data; and
- Fig. 6 is a tabulation of process data.

DETAILED DESCRIPTION

The process of this invention makes use of a unique carrier catalyst system having metallic elements in the form of complex oxides and chlorides impregnated onto a carrier mass, such as alumina, silica, zeolite, or molecular sieve material of such a form as to be suitable for use in a multistage fluidized bed system. The chemical reactions are caused to take place in a series of steps which include:

3

- 1) $2\text{HCl(g)} + 1/2 \text{O}_2\text{(g)} \rightarrow \text{Cl}_2\text{(g)} + \text{H}_2\text{O(g)}$
- 2) $\text{CuO(S)} + \text{HCl(g)} \rightarrow \text{Cu(OH)Cl(S)}$
- 3) $2\text{Cu(OH)Cl(S)} \rightarrow \text{Cu}_2\text{O(S)} + \text{Cl}_2\text{(g)} + \text{H}_2\text{O(g)}$
- 4) $\text{Cu}_2\text{OCl}_2\text{(S)} \rightarrow \text{CuO(S)} + \text{CuCl}_2\text{(S)}$
- 5) $\text{CuCl}_2\text{(S)} \rightarrow \text{CuCl(S)} + 1/2 \text{Cl}_2\text{(g)}$
- 6) $2\text{CuCl(S)} + 1/2 \text{O}_2\text{(g)} \rightarrow \text{CuCl}_2\text{(S)} + \text{CuO(S)}$

These specific steps take place in specific reaction zones and within specific temperature ranges, as described on the block diagram, Fig. 1, and in the following steps:

Step 1. Referring to Fig. 1, the stream 10 of hydrogen chloride, either anhydrous or containing water and process impurities, which might be present, is passed into reactor 11 through a fluidized bed 12 of carrier catalyst of copper oxides and copper chlorides with sodium chlorides, deposited on a suitable carrier in a 1:1 molar ratio. Reactions 2, 3, and 4 for the formation of complex chlorides take place at a temperature maintained in the range of 150° to 220°C. by providing a system 13 of heat transfer within the bed 12, which carries away the exothermic heat of reaction via, in a preferred arrangement, a heat exchanger 14 generating steam to improve the thermal economy of the process.

Chlorinated catalytic material is continuously withdrawn from the first reactor in particulate form and transferred at 40 into the fluidized bed 15 in a second reactor 16 wherein step 2 takes place.

Step 2. In the second reactor, the above reactions 5 and 6 take place to convert the complex chlorides to cupric oxide and release chlorine gas. The fluidized bed in reactor 16 is blown with a gaseous mixture of oxygen and nitrogen ranging from 100% oxygen down to 20% oxygen entering the reactor at 17. The reactor 16 is maintained at a temperature between 300° and 360°C. by means of heat supplied through a system of heat transfer 19 within the fluidized bed.

One of the reactions taking place under the temperature conditions selected is the reverse of reaction (2) above, leading to the formation of a certain amount of hydrogen chloride (see Fig. 3 table) which must be removed from the gas exiting the second reactor, to improve the overall conversion of the feed hydrogen chloride to chlorine, and to avoid contamination of the chlorine product. This removal is accomplished by step 3, the recycle of hydrogen chloride to reactor 11 (see Fig. 5 table). A continuous stream of

SUBSTITUTE SHEET (RULE 26)

carrier catalyst containing cupric oxide is withdrawn through line 41 and returned to bed 12 in the first reactor.

5 Step 3. The total flow of hot gas from the second reactor containing chlorine, oxygen, nitrogen, and some small amount of hydrogen chloride is recycled at 70 through heat exchanger 22 and to the first reactor 11 and the fluidized bed 12, where the contained hydrogen chloride reacts with cupric oxide returned from the second reactor 16 through 41. At the temperature conditions selected for the first fluidized bed 12, 150° to 220°C, only the hydrogen chloride reacts, the oxygen, nitrogen, water, and chlorine passing through without change. See Fig. 5.

10 Step 4. Effluent gases leaving the first reactor at 23 consist of chlorine, water, oxygen, and nitrogen, which pass off to heat exchange at 89, and to recovery system 50, for removal of water at 52, and chlorine product gas at 51. When operated as described, over 99% of the hydrogen chloride 10 entering the system is converted to chlorine product 51.

15 Step 5. In another process step, overall thermal economy can be improved and capital cost can be decreased by adding a third reactor 31 to the system, which includes a fluidized bed 32 of catalytic carrier consisting of complex copper chlorides and sodium salts on a suitable carrier, operating in a temperature range of 350° to 400°C, which reactor is supplied with streams of hydrogen chloride at 10a and oxygen 17a in a continuous flow.

20 Note control valves 71--75 operable to enable step 5.

 In this embodiment, most of the fresh feed hydrogen chloride flows to the third reactor 31 where 60% to 70% of the hydrogen chloride is converted to chlorine and water. Effluent gas at 33 from the third reactor contains chlorine, hydrogen chloride, water, oxygen, and inerts, which controllably passes through valve 75 and joins with the effluent gas 21 from second reactor 16 to flow at 70 through heat exchanger 22 and into first reactor 11 for complete recycle of hydrogen chloride and recovery of chlorine.

25 In this alternate, the third reactor fluidized bed 32 is not circulated but remains constant as a catalyst in the reaction zone for the exothermic reaction, according to equation (1), (see Fig. 6) providing heat through heat exchanger system 34 to drive the endothermic reaction in the second reactor and other high-level energy requirements, such as steam turbines in the overall system, and eliminating the need for a high-temperature combustion system to heat the second reactor.

Experimental work for the further development of this process was carried out to investigate various metallic systems and various carrier masses. The work included tests with manganese, iron and chromium, with sodium and potassium-based promoters. In some tests, the metals used were mixed with copper, as well as used alone. The copper content was varied from 5 to 18 weight percent of the total catalytic carrier mass. As a result of the various experiments, it was concluded that the most consistent and useful catalytic carrier system was copper oxides and copper chlorides blended with equal molar sodium chloride on a zeolite base, which was also suitable for a base material in the fluid catalytic cracking of gas oil in commercial petroleum refineries.

As an illustration of the stream compositions in a combination process for recovery of chlorine from hydrogen chloride, a block flow diagram and material balance is presented in Fig. 2. The calculated streams are based on more than 25 simulated experiments carried out with a one inch diameter by 36 inch long tubular quartz reactor.

As an illustration of the economic factors for the invention, an engineering design was prepared for a plant processing 60,000 tons per year of anhydrous hydrogen chloride and an operating cost was determined based on zero value for the byproduct hydrogen chloride feed. These results, as shown in Fig. 4, indicate a chlorine recovery cost of \$46 per ton (1994 data) with a chlorine selling price of \$230 per ton on the then current market.

Fig. 4 lists process economic factors in terms of typical plant investment and operating cost.

The overall system, as described, provides for essentially 100% conversion of hydrogen chloride to chlorine. The product chlorine can be produced as a liquid or a gas stream of 98% plus purity. No toxic or noxious effluent streams are produced to be released to the atmosphere or ground water. Energy requirements of less than 20% of the standard electrochemical process were realized, as well as significantly less than reported consumptions for alternate proposed chlorine recovery process. Fig. 2 shows material balance data.

The invention also embodies the two reactor process or method set forth below, wherein the designated chlorinator reactor is the same as reactor 11 in Fig. 1, and the designated oxidizer reactor is the same as reactor 16 in Fig. 1.

a) providing at least two reactors, including a chlorinator reactor and an oxidizer reactor, and providing a fluidized bed of a carrier catalyst cupric oxide and cupric chloride in a reaction zone within the chlorinator reactor,

b) supplying a stream of hydrogen chloride to the chlorinator reactor,

5 c) said stream reacting in the chlorinator reactor with said fluidized bed of carrier catalyst cupric oxide and cupric chloride at temperatures between 150° and 220°C, exothermically to convert part of the cupric oxide to cupric chloride, and cupric hydroxychloride, thereby essentially eliminating the hydrogen chloride to produce a product stream including inerts and water, which is removed from the chlorinator reactor, and

10 d) passing a stream of fluidized carrier catalyst containing cupric chloride, cupric hydroxy chloride, and residual cupric oxide from the chlorinator reactor to be supplied to the oxidizer reactor in a bed operating at temperatures between 300° and 380°C, wherein the oxidizer reactor is supplied with oxygen to fluidize the bed, and for endothermic reaction with cupric chloride and cupric hydroxy chloride to produce cupric oxide and a stream of chlorine, hydrogen chloride, inerts and oxygen and,

15 e) feeding the carrier catalyst stream containing cupric oxide to the oxidizer reactor for reaction with hydrogen chloride, as defined in c), and

f) supplying the stream of chlorine, hydrogen chloride, inerts and oxygen from the oxidizer reactor to the chlorinator reactor to cause the hydrogen chloride portion of the stream to react with the cupric oxide in the carrier catalyst at the operating temperature between 150° and 220°C,

20 g) the product stream from the chlorinator reactor being chlorine rich but substantially free of hydrogen chloride,

25 h) and wherein heat generated in the chlorinator reactor can be optionally used to supply heat for process use.

The invention also embodies the three reactor process or method as set forth below, wherein the described first reactor is the same as reactor 31 in Fig. 1; the designated second reactor is the same as reactor 11 in Fig. 1; and the designated third reactor is the same as reactor 16 in Fig. 1:

30 a) providing first, second and third reactors, and providing a fluidized bed of a carrier catalyst cupric oxide and cupric chloride in a reaction zone within the second reactor,

b) supplying hydrogen chloride and oxygen to react exothermically in the first reactor to produce a stream of chlorine and water, at elevated temperatures between 300° and 400°C, and also unreacted hydrogen chloride and oxygen which is removed from the first reactor and flow to the second reactor and,

c) the stream reacting in the second reactor with the fluidized bed of carrier catalyst cupric oxide and cupric chloride at temperatures between 150° and 220°C. exothermically to convert part of the cupric oxide to cupric chloride, and cupric hydroxychloride, thereby essentially eliminating the hydrogen chloride to produce a product stream of chlorine, water, inerts and oxygen which is removed from the second reactor, and

d) passing a stream of the fluidized carrier catalyst containing cupric chloride, cupric hydroxy chloride, and residual cupric oxide from the second reactor to be supplied to the third reactor in a bed operating at temperatures between 300° and 380°C, wherein the third reactor is supplied with oxygen to fluidize the bed, and for endothermic reaction with cupric chloride and cupric hydroxy chloride to produce cupric oxide and a stream of chlorine, hydrogen chloride and oxygen and,

e) feeding the carrier catalyst stream containing cupric oxide to the second reactor for reaction with hydrogen chloride, as defined in c), and

f) supplying the stream of chlorine, hydrogen chloride, inerts and oxygen from the third reactor to the second reactor to cause the hydrogen chloride component of that stream to react with the cupric oxide in the carrier catalyst at operating temperatures between 150° and 220°C, and

g) the product stream from the second reactor which contains chlorine, water and oxygen being chlorine rich but substantially free of hydrogen chloride,

h) and wherein heat generated in the first reactor exothermic reaction can be optionally used to supply heat for process use.

In the above, the reactor 16 may be divided into two temperature zones. A gas stream from the hot zone at temperatures between 300° and 380°C. passes through the fluidized catalytic carrier maintained at between 150° and 220°C, to cause the hydrogen chloride present in the gas to react with the cupric oxide in the catalytic carrier, thereby producing an effluent product stream which contains chlorine, oxygen and water but is free of hydrogen chloride.

As stated in the disclosure of U.S. Patent 4,959,202, the processes can be carried out using a catalytic carrier where manganese oxides and chlorides are substituted

for copper, with good results, where a chlorination temperature in the range of 250°-350°C, and an oxidation temperature of about 400°-450°C.

Iron oxides and chlorides can also be substituted.

Heat recovery and chlorine recovery from the product stream can be carried out as described in U.S. Patent 4,959,202.

WE CLAIM:

1. In a process of recovering chlorine from a stream of hydrogen chloride, the steps that include:

a) providing at least two reactors, including a chlorinator reactor and an oxidizer reactor, and providing a fluidized bed of a carrier catalyst cupric oxide and cupric chloride in a reaction zone within the chlorinator reactor,

b) supplying a stream of hydrogen chloride to the chlorinator reactor,

c) said stream reacting in the chlorinator reactor with said fluidized bed of carrier catalyst cupric oxide and cupric chloride at temperatures between 150° and 220°C, exothermically to convert part of the cupric oxide to cupric chloride, and cupric hydroxychloride, thereby essentially eliminating the hydrogen chloride to produce a product stream including inerts and water, which is removed from said chlorinator reactor, and

d) passing a stream of said fluidized carrier catalyst containing cupric chloride, cupric hydroxy chloride, and residual cupric oxide from said chlorinator reactor to be supplied to the oxidizer reactor in a bed operating at temperatures between 300° and 380°C, wherein said oxidizer reactor is supplied with oxygen to fluidize said bed, and for endothermic reaction with cupric chloride and cupric hydroxy chloride to produce cupric oxide and a stream of chlorine, hydrogen chloride, inerts and oxygen and,

e) feeding said carrier catalyst stream containing cupric oxide to the oxidizer reactor for reaction with hydrogen chloride, as defined in c), and

f) supplying the stream of chlorine, hydrogen chloride, inerts and oxygen from the oxidizer reactor to the chlorinator reactor to cause the hydrogen chloride portion of the stream to react with the cupric oxide in the carrier catalyst at the operating temperature between 150° and 220°C.,

g) said product stream from the chlorinator reactor being chlorine rich but substantially free of hydrogen chloride,

h) and wherein heat generated in the chlorinator reactor can be optionally used to supply heat for process use.

2. The method of claim 2 wherein the oxidized reactor is divided into two temperature zones, and wherein a gas stream from the hot zone at temperatures between 300° and 380°C. passes through the fluidized catalytic carrier maintained at between 150° and 220°C., to cause the hydrogen chloride present in the gas to react with the cupric oxide

in the catalytic carrier, thereby producing an effluent product stream which contains chlorine, oxygen and water but is free of hydrogen chloride.

3. The method of claim 1 wherein said cupric oxide in said stream defined in e) of claim 1 is removed from said oxidizer reactor.

5 4. The method of claim 1 including supplying heat to said oxidizer reactor.

5. The method of claim 1 including removing chlorine from said product stream.

10 6. The method of claim 1 wherein said heat generated in the chlorinator reactor is supplied to said oxidizer reactor.

7. The method of claim 1 wherein said catalytic carrier is selected from the group consisting of alumina, zeolite, silica, and molecular sieve material.

15 8. The method of claim 1 including transferring heat from the stream of chlorine, hydrogen chloride, inerts, and oxygen flowing from the oxidizer reactor to the chlorinator reactor.

9. The method of claim 1 including controlling the supply of hydrogen chloride and oxygen to the reactors.

10. In a process of recovering chlorine from a stream of hydrogen chloride, the steps that include:

20 a) providing first, second and third reactors, and providing a fluidized bed of a carrier catalyst cupric oxide and cupric chloride in a reaction zone within the second reactor,

25 b) supplying hydrogen chloride and oxygen to react exothermically in the fluidized bed of carrier catalyst cupric chloride, and cupric oxide in the first reactor to produce a stream of chlorine and water, at elevated temperatures between 300 and 380°C.,

and also unreacted hydrogen chloride and oxygen which is removed from the first reactor and flow to the second reactor and,

c) said stream reacting in the second reactor with said fluidized bed of carrier catalyst cupric oxide and cupric chloride at temperatures between 150° and 220°C. exothermically to convert part of the cupric oxide to cupric chloride, and cupric hydroxychloride, thereby essentially eliminating the hydrogen chloride to produce a product stream of chlorine, water, inerts and oxygen which is removed from said second reactor, and

d) passing a stream of said fluidized carrier catalyst containing cupric chloride, cupric hydroxy chloride, and residual cupric oxide from said second reactor to be supplied to said third reactor in a bed operating at temperatures between 300° and 380°C, wherein said third reactor is supplied with oxygen to fluidize said bed, and for endothermic reaction with cupric chloride and cupric hydroxy chloride to produce cupric oxide and a stream of chlorine, hydrogen chloride and oxygen and,

e) feeding said carrier catalyst stream containing cupric oxide to the second reactor for reaction with hydrogen chloride, as defined in c), and

f) supplying the stream of chlorine, hydrogen chloride, inerts and oxygen from the third reactor to the second reactor to cause the hydrogen chloride component of that stream to react with the cupric oxide in the carrier catalyst at said operating temperatures between 150° and 220°C., and

g) said product stream from the second reactor which contains chlorine, water and oxygen being chlorine rich but substantially free of hydrogen chloride,

h) and wherein heat generated in the first reactor exothermic reaction can be optionally used to supply heat for process use.

11. The method of claim 10 wherein the third reactor is divided into two temperature zones, and wherein a gas stream from the hot zone at temperatures between 300° and 380°C. passes through the fluidized catalytic carrier maintained at between 150° and 220°C. to cause the hydrogen chloride present in the gas to react with the cupric oxide.

in the catalytic carrier, thereby producing an effluent product stream which contains chlorine, oxygen and water but is free of hydrogen chloride.

12. The method of claim 10 wherein said cupric oxide in said stream defined in e) of claim 10 is removed from said third reactor.

5 13. The method of claim 10 including supplying heat to said oxidizer reactor.

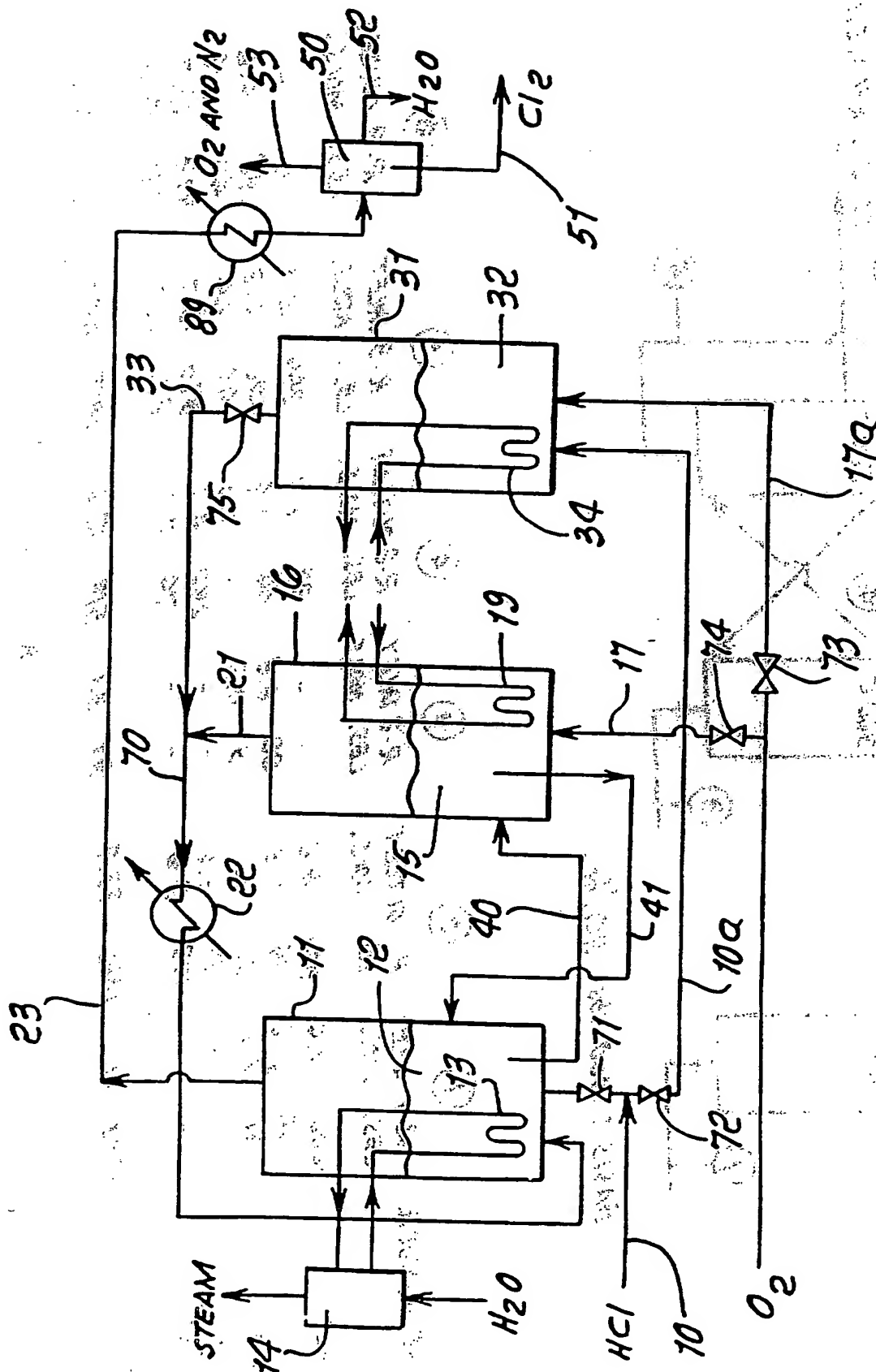
14. The method of claim 10 including removing chlorine from said product stream.

10 15. The method of claim 10 wherein said heat generated in the first reactor is supplied to said third reactor.

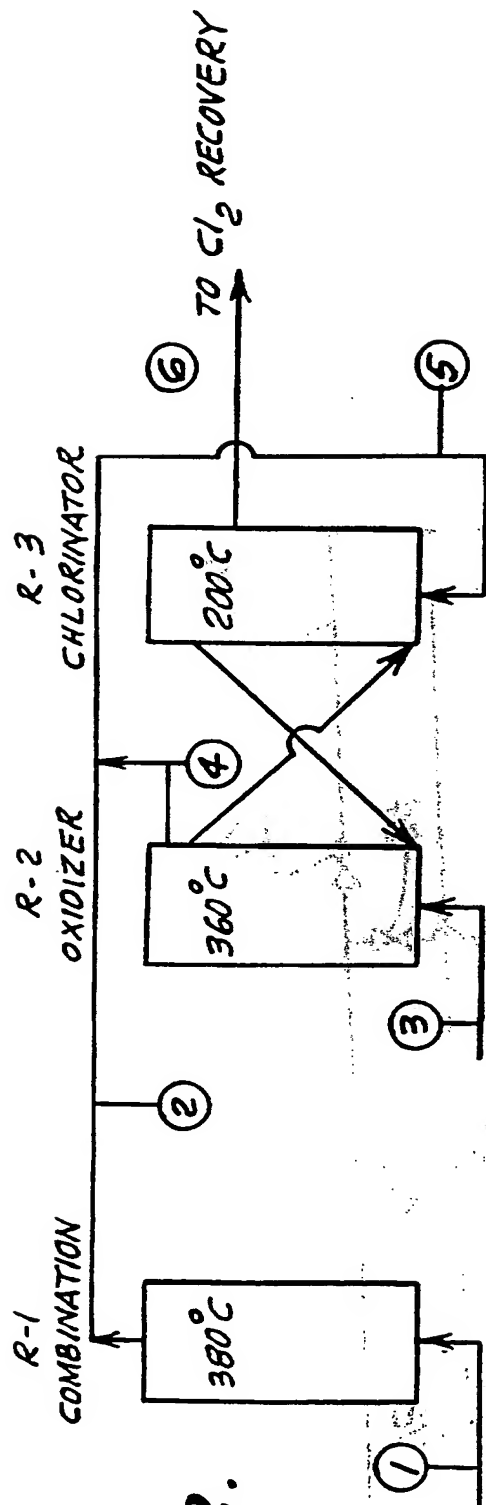
16. The method of claim 10 including transferring heat from the third reactor to the second reactor.

17. The method of claim 10 including controlling the supply of hydrogen chloride and oxygen to the reactors.

FIG. 1.



SUBSTITUTE SHEET (RULE 26)



BASIS : 1000 lbs. HCl/hr.

LINE NUMBER	① R-1 INLET LBS. MOLS.	② R-1 OUTLET LBS. MOLS.	③ R-2 INLET LBS. MOLS.	④ R-2 OUTLET LBS. MOLS.	⑤ R-3 INLET LBS. MOLS.	⑥ R-3 OUTLET LBS. MOLS.
HCl	1000	27.4	300	8.2	-	-
O2	308	9.6	154	4.8	88	2.8
N2	31	1.1	31	1.1	9	0.3
Cl2	-	-	681	9.6	-	-
H2O	-	-	173	9.6	74	4.1
TOTALS	1339	40.1	1339	33.3	97	3.1
				518	12.6	1859
					45.9	1556
						40.5

3/6

FIG. 3

CHLORINATION STEP

FLOW RATE: 180 ml/min HCl
300 ml/min NITROGEN

TEMPERATURE 240° C
TIME 5 MINUTES

CHLORINATION

MOLAR INPUT
HCl

0.042

OXIDATION STEP

FLOW RATE: 300 ml/min OXYGEN
150 ml/min NITROGEN

TEMPERATURE 360° C
TIME 20 MINUTES

OXIDATION

MOLAR OUTPUT
CHLORINE

0.01518

MOLAR OUTPUT
HCl

0.01343

% MASS Cl
BALANCE

100

FIG. 4.

<u>PLANT INVESTMENT</u>	<u>\$ MM</u>
CATALYTIC CARRIER COMBINATION, OXIDIZER AND CHLORINATOR UNIT	3.5
ASSOCIATED EQUIPMENT AND Cl ₂ RECOVERY SYSTEMS	2.5
SCRUBBERS, REFRIGERATION AND STORAGE, WASTE HEAT RECOVERY, STEAM GENERATION, UTILIZATION AND MISCELLANEOUS	1.8
	1.0
TOTAL (BATTERY LIMITS COSTS)	<u>8.8</u>

<u>OPERATING COST</u>	<u>\$/TON PRODUCT Cl₂</u>
CAPITAL @ 20%	30
UTILITIES (FUEL AND POWER)	2
CHEMICALS AND CATALYSTS	3
LABOR AND OVERHEAD	4
MAINTENANCE @ 5%	7
	<u>46</u>

Fig. 5.

CHLORINATOR TEMP. 200°C
FLOW TIME: 5 MINUTES (REPEATED 10 TIMES)

	INLET FLOW RATES MILLILITERS/MINUTES		MOLES INPUT	MOLES OUTPUT
A.	Cl ₂	215	0.048	0.048
	HCl	200	0.045	0.001
	O ₂	100	0.023	0.023
	N ₂	20	0.005	0.005
B.	HCl	200	0.045	0.0004
	O ₂	200	0.045	0.045
	N ₂	100	0.023	0.023
C.	HCl	200	0.045	0.0004
	N ₂	300	0.068	0.068

Fig. 6.

FLOW RATE ML/MIN.	TEMP. C	TIME MIN.	<u>MOLES COLLECTED</u>		<u>% HCl CONVERSION</u>
			<u>HCl MOLES</u>	<u>CHLORINE MOLES</u>	
800 OXYGEN 200 HCl	360	15	0.031	0.042	73
600 OXYGEN 200 HCl	360	15	0.036	0.041	69
400 OXYGEN 200 HCl	360	15	0.044	0.036	62
200 OXYGEN 200 HCl	360	15	0.049	0.032	57
400 OXYGEN 400 HCl	360	15	0.146	0.038	34
300 OXYGEN 180 HCl 100 NITROGEN	360	15	0.042	0.037	64
100 OXYGEN 100 HCl 400 NITROGEN	360	60	0.054	0.090	77

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/14736

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 7/04, 7/07

US CL : 423/502,507,493,604

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/502,507,493,604

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
noneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,959,202 (MINET ET AL) 25 September 1990, claims 1, 8, col. 3, lines 27-33, col. 6, lines 53-56, Fig. 2.	1-17
Y	US, A, 2,542,961 (JOHNSON ET AL) 20 February 1951, claim 1, col. 4, lines 11-14 and 65-71.	1-17
Y	US, A, 2,448,255 (BENEDICTIS ET AL) 31 August 1948, col. 2, lines 30-42.	10-17
A	US, A, 3,332,742 (METAIZEAU), 25 July 1967.	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be of particular relevance
* E	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* L	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* O		document referring to an oral disclosure, use, exhibition or other means
* P	* A	document member of the same patent family
		document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search

30 DECEMBER 1995

Date of mailing of the international search report

09 FEB 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

NGOC-YEN NGUYEN

Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☒ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)